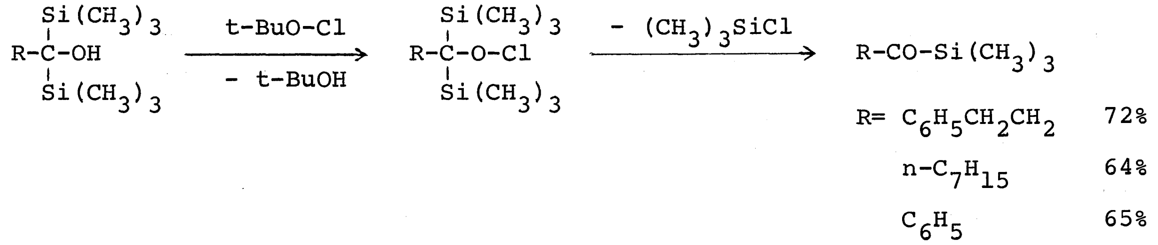
CHEMISTRY LETTERS, pp. 993-994, 1976. Published by the Chemical Society of Japan

AN EFFICIENT METHOD FOR THE PREPARATION OF ACYLSILANE AND α-HALOACYLSILANE

Isao KUWAJIMA, Toru ABE, and Naoki MINAMI
Department of Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

On treating 1,1-bis(trimethylsilyl)alkan-1-ol with t-butyl hypochlorite, the corresponding acylsilane is obtained in good yield, while the reaction of the alcohol with NBS, in contrary, affords α-bromoacylsilane exclusively.

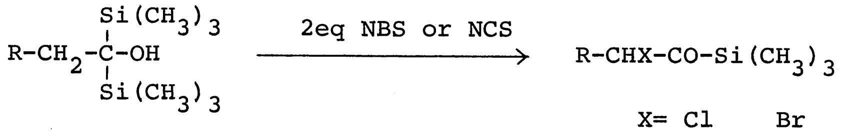
Acylsilane is well known to exhibit an interesting spectral behavior[1] and several methods have been devised for its preparation. Among them reported hitherto, the most effective procedures involve an initial generation of acyl anion equivalent such as 2-lithio-1,3-dithiane[2] or 1-ethoxyvinyllithium[3] followed by treating with trialkylsilyl chloride and removal of the protecting group, since other methods suffer from disadvantages such as structural limitation[4] or low efficacies.[5] However, for large scale preparation, the methods utilizing acyl anion equivalents do not appear to be adequate because of rather expensive reagents. We wish to report herein another efficient method which seems to be useful for such purpose because of simplicity in the procedure and use of inexpensive reagents. We have recently reported that 1,1-bis(trimethylsilyl)alkan-1-ol can be prepared effectively from the corresponding trimethylsilyl carboxylate via reductive silylation.[6] During studies on the oxidation of this type of alcohol, it has proved to be a good precursor of acylsilane. For example, treatment of the alcohol with t-butyl hypochlorite leads to the formation of the corresponding acylsilane in good yield as shown in the following equation.



$$R\text{-}\overset{\overset{\displaystyle Si(CH_3)_3}{|}}{\underset{\underset{\displaystyle Si(CH_3)_3}{|}}{C}}\text{-}OH \xrightarrow[-\ t\text{-}BuOH]{t\text{-}BuO\text{-}Cl} R\text{-}\overset{\overset{\displaystyle Si(CH_3)_3}{|}}{\underset{\underset{\displaystyle Si(CH_3)_3}{|}}{C}}\text{-}O\text{-}Cl \xrightarrow{-\ (CH_3)_3SiCl} R\text{-}CO\text{-}Si(CH_3)_3$$

R=	
$C_6H_5CH_2CH_2$	72%
$n\text{-}C_7H_{15}$	64%
C_6H_5	65%

On the other hand, when N-bromosuccinimide(NBS) was employed in place of t-butyl hypochlorite, the acylsilane initially formed is found to react further with the oxidizing agent to afford the corresponding α-bromoacylsilane exclusively. Bromination of the acylsilane with NBS seems to proceed much faster than the oxidation of the alcohol. Thus, the bromide and the recovered alcohol were isolated but non-brominated acylsilane was not obtained even if the reaction was attempted by using equimolar amount of NBS. Similarly, the reaction with N-chlorosuccinimide gave the corresponding α-chloroacylsilane in moderate yield.



$$R\text{-}CH_2\text{-}\overset{Si(CH_3)_3}{\underset{Si(CH_3)_3}{C}}\text{-}OH \xrightarrow{\text{2eq NBS or NCS}} R\text{-}CHX\text{-}CO\text{-}Si(CH_3)_3$$

	X= Cl	Br
R= $C_6H_5CH_2$	47%	61%
$n\text{-}C_6H_{13}$	--	71%

The following examples are illustrative.

3-Phenylpropionyltrimethylsilane.[7] To neat t-butyl hypochlorite (123 mg, 1.1 mmol) was added 2 ml carbon tetrachloride solution of 1,1-bis(trimethylsilyl)-3-phenylpropan-1-ol (280 mg, 1.0 mmol) at 0°. After it was stirred for 4 hr at 0°, the reaction mixture was quenched with aq $NaHCO_3$. 3-Phenylpropinyltrimethylsilane (151 mg, 72%), ir(neat); 1638 (C=O), 1250 (C-Si) and 845 cm^{-1}(C-Si), nmr (CCl_4); δ 0.23 (s, 9H, $(C\underline{H}_3)_3Si$), 2.90 (s, 4H, $C_6H_5C\underline{H}_2C\underline{H}_2C=O$), and 7.17 (s, 5H, aromatic proton), was obtained along with the recovered alcohol (40 mg, 14%) after removal of the solvents from the ether extracts followed by silica gel chromatography.

2-Chloro-3-phenylpropionyltrimethylsilane.[8] A solution of 1,1-bis(trimethylsilyl)-3-phenylpropan-1-ol (280 mg, 1.0 mmol) was added to a suspended solution of N-chlorosuccinimide (334 mg, 2.5 mmol) in 2 ml carbon tetrachloride and the mixture was stirred for 20 hr at room temperature. After the reaction mixture had been worked up similarly as above, the title compound, ir(neat); 1655 (C=O), 1255 (C-Si) and 850 cm^{-1}(C-Si), nmr(CCl_4); δ 0.33 (s, 9H, $(C\underline{H}_3)_3Si$), 2.95 (d.d, J_{gem}= 14 Hz, J_{vic}= 8 Hz, 1H, $C_6H_5C\underline{H}_2CHClC=O$), 3.40 (d.d, J_{gem}= 14 Hz, J_{vic}= 6 Hz, 1H, $C_6H_5C\underline{H}_2CHClC=O$), 4.50 (d.d, J_{vic}= 8 and 6 Hz, 1H, $C_6H_5CH_2C\underline{H}ClC=O$), and 7.20 (s, 5H, aromatic proton), was obtained in 47% yield.

References and Notes

1. A. G. Brook, Advan. Organometal Chem., 7, 95 (1968).
2. A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, J. Am. Chem. Soc., 89, 431 (1967); E. J. Corey, D. Seebach, and R. Freedman, ibid., 89, 434 (1967).
3. E. M. Dexheimer and L. Spialter, J. Organomet. Chem., 107, 229 (1976).
4. G. J. D. Peddle, ibid., 14, 139 (1968); P. Bourgeois, ibid., 76, C1 (1974); J. Dunogues, M. Bolourtchian, R. Calas, N. Duffaut, and J. P. Picard, ibid., 43, 157 (1972).
5. P. Bourgeois, J. Dunogues, and N. Duffaut, ibid., 80, C25 (1974).
6. I. Kuwajima, T. Sato, N. Minami, and T. Abe, Tetrahedron Lett., 1591 (1976).
7. The structure of the product was further confirmed by comparison with the authentic sample prepared by the method using 2-lithio-1,3-dithiane.[2]
8. Analytical sample for elemental analysis could not be obtained for this product, because it was too unstable to be distilled. The structure of the product was confirmed by converting it into the corresponding α-phenylthioacylsilane.

(Received July 27, 1976)